

# Test of the semischematic model for a liquid of linear molecules

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We apply to a liquid of linear molecules the semischematic mode-coupling model, previously introduced to describe the center of mass (COM) slow dynamics of a network-forming molecular liquid. We compare the theoretical predictions and numerical results from a molecular dynamics simulation, both for the time and the wave-vector dependence of the COM density-density correlation function. We discuss the relationship between the presented analysis and the results from an approximate solution of the equations from molecular mode-coupling theory [R. Schilling and T. Scheidsteiger, *Phys. Rev. E* **56** 2932 (1997)].

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## I. INTRODUCTION

The mode-coupling theory (MCT) [1,2] has opened new perspectives in the theoretical understanding of the dynamic slowing down characteristic of supercooled glass-forming liquids [3]. MCT, originally developed to describe the structural relaxation in simple liquids, i.e. in liquids composed by particles interacting via spherically symmetric intermolecular potentials, also offers a coherent picture of the slow dynamics in molecular glass forming liquids, composed of asymmetric molecules. The ability of MCT to model the onset of slow dynamics in molecular liquids has prompted the need to extend the theory to fully take into account the angular degrees of freedom. The extension of MCT to a solute linear molecule in a solvent of spherical particles [4] and to molecular liquids [5,6], which we refer to in the following as molecular MCT (MMCT), has been recently achieved. The center of mass (COM) density-density correlation function, which in MCT is the only relevant correlation function, in MMCT becomes coupled to an infinite hierarchy of rotational correlation functions, arising from the expansion of the angular degrees of freedom in spherical harmonics. The MMCT equations for COM and angular correlators have been solved until now for systems of linear molecules under specific approximations [5–7]. Work is currently underway to improve the approximations for dumbbells and to calculate a solution for the general case of molecules of arbitrary shape.

Recently, some of us proposed a parameterization of the role of the rotational degrees of freedom and their effective coupling with the COM density [8]. This approach, which provides a solvable set of coupled equations for the slow dynamics of the COM density-density correlation function, has been named *semischematic* because it retains all the  $q$ -dependence of the COM correlators but condenses the coupling between COM and

angular correlation functions into a single  $q$ -independent parameter  $\chi_R$ . A detailed comparison between the theoretical predictions of the model and results from a molecular dynamics (MD) simulation has been performed for a network forming liquid [8], finding an excellent agreement up to a cut-off  $q$ -vector value where the microscopic geometric details become dominant.

In the long term, the exact solutions of the MMCT equations are to be preferred because they do not require an *ad hoc* estimate of the translational-rotational coupling and predict also the behavior of the angular correlators. On the other hand, in the short term the semischematic equations are rather appealing because of their simplicity, for the minimal amount of input information required and because the complete time dependent solution can be achieved with present day computational facilities. Also, once the ability of the semischematic model to describe the time evolution of the COM correlation functions has been assessed by detailed comparison with MD simulations, comparison with experimental data is foreseeable, again due to the limited need for structural input. For this reason, in this Article we solve the semischematic model for a system of linear dumbbells interacting through a Lennard-Jones (LJ) potential and compare the predictions of the model with the corresponding quantities evaluated from long MD simulations of the same liquid [9]. The choice of a liquid of dumbbells for which the MMCT equations have been previously solved approximately [7] allows at the same time a comparative discussion of the two theoretical methods.

## II. THEORY

The semischematic model is defined by introducing in the ideal MCT equations for simple liquids an effective coupling parameter  $\chi_R$  which models the caging effect of the molecular rotational motion on the COM dynam-

ics, i.e. the slowing down of the COM relaxation introduced by the angular degrees of freedom. The resulting system of integro-differential equations [8] describes the time evolution of the normalized density-density COM correlation functions  $\phi_q(t) = S_q(t)/S_q$ ,  $S_q(t)$  being the dynamic structure factor

$$S_q(t) = \frac{1}{N} \langle \rho_q(t)^* \rho_q(0) \rangle \quad (1)$$

and  $S_q = S_q(0)$  the static structure factor. The unknown  $\chi_R$  is fixed once and for all by requiring that the ideal glass transition temperature in the model  $T_c^{MCT}$  coincides with the temperature calculated from the analysis of experimental or MD data. The imposed equality of the theoretical and MD temperatures is very important because it allows to compare the numerical and the MD data at the same reference  $T$ , i.e. with the same structure factor and the same thermal broadening [10]. A larger value of  $\chi_R$  corresponds to a stronger slowing down of the COM relaxation due to the interaction with the rotational motion. If  $\chi_R = 1$  the semischematic model coincides with the standard MCT [1].

The physics described by the semischematic model is the same as for the ideal MCT. It predicts that when  $T < T_c^{MCT}$ ,  $\phi_q(t)$  does not relax to zero at long times and the COM dynamics is frozen. Above  $T_c^{MCT}$  the correlator  $\phi_q(t)$  decays with a typical two step relaxation process, characterized by the fast decay to a plateau value (the non ergodicity parameter) followed by a slow relaxation to zero which gets slower and slower as  $T_c^{MCT}$  is approached ( $\alpha$ -relaxation).

The semischematic model describes the dynamic evolution of  $\phi_q(t)$  in the time region where the slow dynamics becomes dominant ( $\alpha$ -region) by the system of coupled equations

$$\phi_q(\hat{t}) = m_q(\hat{t}) - \frac{d}{d\hat{t}} \int_0^{\hat{t}} ds m_q(\hat{t} - s) \phi_q(s) \quad (2)$$

where the time variable  $\hat{t}$  is defined in terms of a characteristic time scale which diverges at  $T_c^{MCT}$  [1]. The *memory function*  $m_q$  is a quadratic functional of the correlations  $\phi_q(t)$  themselves

$$m_q[\phi_k(t)] = \frac{\chi_R}{2} \int \frac{d^3k}{(2\pi)^3} V(\vec{q}, \vec{k}) \phi_k(t) \phi_{|\vec{q}-\vec{k}|}(t) \quad (3)$$

and its increase on cooling is responsible for the slowing down of the relaxation process. The parameter  $\chi_R$  enters in Eq. 3 as a  $q$ -independent multiplicative factor, thus increasing the strength of the COM memory function.

The vertices in Eq. 3 are defined as

$$V(\vec{q}, \vec{k}) \equiv S_q S_k S_{|\vec{q}-\vec{k}|} \frac{1}{nq^4} \left[ \vec{q} \cdot \vec{k} (1 - S_k^{-1}) + \vec{q} \cdot (\vec{q} - \vec{k}) (1 - S_{|\vec{q}-\vec{k}|}^{-1}) \right]^2 \quad (4)$$

and are functions of the COM  $S_q$  and inversely proportional to the density.

The infinite time limit  $f_q$  of  $\phi_q(t)$  can be calculated solving self-consistently on a discrete set of  $q$  values the coupled integral equations

$$\frac{f_q}{(1 - f_q)} = m_q[f_k] \quad (5)$$

using as input the number density  $n$  and  $S_q$  which can be calculated from the MD data or measured experimentally.

Having chosen  $\chi_R$  properly, at the ideal glass transition temperature the solution  $f_q$  of Eq. 5 jumps discontinuously from zero to a nonzero value, which defines the non ergodicity parameter  $f_q^c$  [1,2]. In what follows we will neglect the upper index in the non ergodicity parameter.

In the supercooled liquid phase, after the plateau  $f_q$ ,  $\phi_q(t)$  follows an initial power law decay (von Schweidler law), ruled by a  $q$  independent scaling exponent  $b$ , followed by a stretched exponential relaxation (Kohlrausch-William-Watts law):

$$\phi_q(t) \sim A_q^K \exp \left[ - \left( \frac{t}{\tau_q^K} \right)^{\beta_q^K} \right] \quad (6)$$

The range of validity of the von Schweidler law is strongly  $q$  dependent [11] and, therefore, it is worthwhile to consider also the second order corrections:

$$\phi_q(t) \sim f_q - h_q^{(1)} \left( \frac{t}{\tau} \right)^b + h_q^{(2)} \left( \frac{t}{\tau} \right)^{2b} + O((t/\tau)^{3b}) \quad (7)$$

The exponent  $b$  can be calculated solving

$$\lambda = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)} \quad (8)$$

where  $\Gamma$  is the Euler gamma function and the *exponent parameter*  $\lambda$  is defined by

$$\lambda \equiv \frac{1}{2} \int_0^\infty dq \int_0^\infty dk \int_0^\infty dp \hat{e}_q^c (1 - f_k)^2 e_k^c \frac{\delta^2 m_q}{\delta f_k \delta f_p} (1 - f_p)^2 e_p^c \quad (9)$$

In Eq. 9  $e^c$  and  $\hat{e}^c$  are the right and left eigenvector corresponding to the maximum eigenvalue of the stability matrix

$$C_{qk}^c[f_p] \equiv \frac{\delta m_q[f_p]}{\delta f_k} (1 - f_k)^2 \quad (10)$$

evaluated at the critical point. The critical amplitude  $h_q^{(1)}$  is

$$h_q^{(1)} = (1 - f_q)^2 e_q^c \quad (11)$$

while  $h_q^{(2)}$  can be calculated as explained in Ref. [11].

In Sec. IV we compare the predictions of the semischematic model for the slow relaxation in a liquid of linear molecules with the corresponding predictions of MMCT. To facilitate the reading of the present Article we present here a brief outline of the MMCT for linear molecules. We refer the interested reader to Refs. [5–7].

According to MMCT the relevant variables for the description of the slow dynamics of supercooled molecular glass forming liquids are the generalized correlation functions

$$S_{ll'}^m(q, t) = \frac{1}{N} \langle \rho_{lm}(q, t)^* \rho_{l'm}(q, 0) \rangle \quad (12)$$

where the density functions are defined by

$$\rho_{lm}(\vec{q}, t) = i^l \sqrt{4\pi} \sum_{j=1}^N e^{i\vec{q} \cdot \vec{x}_j(t)} Y_{lm}(\Omega_j(t)) \quad (13)$$

In Eq. 13 the sum runs over the  $N$  molecules of the liquid,  $\vec{x}_j$  is the COM position of the  $j$ th molecule and  $Y_{lm}(\Omega_j)$  are the spherical harmonics for its Euler's angles. The index  $l$  ranges over the whole set of nonnegative integer numbers, while  $m \in [-l, l]$ . For  $l = l' = 0$  the correlation function defined in Eq. 12 coincides with the COM correlator  $S_q$  studied by the usual MCT and the semischematic model. Due to the lack of rotational invariance of the molecules the correlation functions depend both on modulus and orientation of the wave vector. In Eq. 12 we have chosen a reference frame where  $\vec{q}$  points in the direction of the  $z$  axes, which offers the advantage of diagonality of the correlators with respect to  $m$ . The evolution equations for the correlators in Eq. 12 are a generalization of Eq. 2 for a single  $q$  dependent correlator. The slowing down of the relaxation is ruled by a infinite set of memory functions  $[M_{ll'}^m(q, t)]^{\alpha\alpha'}$  which are quadratic functionals of the whole set of correlators (12). The extra indices  $\alpha, \alpha' \in \{T, R\}$  are related to projection operations on the longitudinal translational ( $T$ ) and rotational ( $R$ ) currents. For the aims of this Article we underline that in MMCT the time evolution of each correlator is coupled, through the memory functions, to every other correlator. This means that, due to the dependence of  $[M_{00}^0(q, t)]^{TT}$  on both the translational and rotational correlators, the dynamics of the COM correlator  $S_{00}^0(q, t)$  is affected by the time evolution of every angular correlation function  $S_{ll'}^m(q, t)$  with  $l \neq 0$ .

With the cut-off  $l \leq 2$ , the non ergodicity parameters  $f_{ll}^m(q) = \lim_{t \rightarrow \infty} S_{ll}^m(q, t)/S_{ll}^m(q)$  have been calculated for the liquid of LJ dumbbells in the approximation of diagonality in  $l$ , i.e.  $S_{ll'}^m(q, t) \approx \delta_{ll'} S_{ll}^m(q, t)$  and  $[M_{ll'}^m(q, t)]^{\alpha\alpha'} \approx \delta_{ll'} [M_{ll}^m(q, t)]^{\alpha\alpha'}$  [7]. We stress that this diagonality was also demanded for the static correlators  $S_{ll}^m(q)$ , in order to keep the MMCT-equations as simple as possible. The input of the calculations are the number density of molecules and all the static structure factors

$S_{ll}^m(q)$  up to  $l = 2$  as evaluated from the set of MD data [9]. In Fig. 1 we show the results (from Ref. [6]) for the COM non ergodicity parameter  $f_{00}^0$  at two different temperatures (short and long dashed lines). The higher one,  $T_t^{MMCT} = 0.383$ , corresponds to the MMCT theoretical freezing temperature for the translational degrees of freedom, i.e. at  $T_t^{MMCT}$  the COM  $f_{00}^0$  jumps to a non zero value while the rotational dynamics is still in a liquid phase. At the lower temperature  $T_r^{MMCT} = 0.310$  all the other non ergodicity parameters  $f_{ll}^m$  ( $l \neq 0$ ) become nonzero, i.e.  $T_r^{MMCT}$  is the MMCT theoretical transition temperature for the rotational dynamics. This splitting of critical temperatures, not observed in the simulation, is an artifact of the diagonalization approximation and is not observed when the approximation  $l \neq l'$  is waived [12].

### III. MODEL AND SIMULATION DATA

The model under investigation is an one-component system containing  $N = 500$  rigid diatomic molecules. Each molecule consists of two atoms, labeled A and B, separated by a distance  $d$ . The interaction between two molecules is build up by pair interactions between the atoms, which are due to the LJ potentials

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right] \quad \alpha, \beta \in \{A, B\} \quad (14)$$

with LJ parameters  $\epsilon_{AA} = \epsilon_{AB} = 1.0, \epsilon_{BB} = 0.8$  and  $\sigma_{AA} = \sigma_{AB} = 1.0, \sigma_{BB} = 0.95$ , i.e.  $\epsilon_{AA}$  was chosen as the unit of energy and temperature ( $k_B = 1$ ) and  $\sigma_{AA}$  as the unit of length. The unit of time is then  $((\sigma_{AA}^2 m)/(48\epsilon_{AA}))^{\frac{1}{2}}$  where  $m$  is the mass of an atom which is chosen to be equal for both types of atoms. The slight head-tail asymmetry of the dumbbell assures, together with the choice of  $d = 0.5$  as inter-atomic distance, a good coupling between translational and rotational motion on the one hand and avoids crystallization into a liquid crystalline phase and the intersection of two dumbbells on the other.

After equilibrating the system in the (N,p,T)-ensemble for times which exceeded the relaxation times of the system even at the lowest temperature, the production runs were carried out in the microcanonical ensemble. To improve the statistics the data for each temperature were averaged over at least 8 independent runs. Further details about the simulation can be found in the references [9] from which we take part of the data to be compared with the theoretical results.

The critical temperature for the COM which was determined from the simulation by fitting the  $\alpha$ -relaxation-time and the diffusion constant  $D$  with power laws

$$\tau \propto (T - T_c)^{-\gamma} \quad , \quad D \propto (T - T_c)^\gamma \quad (15)$$

according to MCT predictions, was found to be  $T_c^{MD} = 0.477$ . The numerical values for the non ergodicity parameter  $f_q$ , the critical amplitude  $h_q^{(1)}$  and the second order correction  $h_q^{(2)}$  at the critical temperature  $T^{MD} = 0.477$  are also taken from reference [9]. They were evaluated by fitting the decay from the plateau in  $\phi_q(t)$  with the von Schweidler law Eq. 7, including the second order correction. From the same procedure the critical exponent  $b = 0.55$  is also obtained and, via Eq.8, one gets for the exponent parameter  $\lambda$  the result  $\lambda = 0.76$ . Furthermore we have examined the time dependence of the MD correlator  $\phi_q(t)$  in the  $\alpha$ -region by evaluating the amplitudes  $A_q^K$ , stretching exponents  $\beta_q^K$  and relaxation times  $\tau_q^K$  of a Kohlrausch–Williams–Watts fit (Eq. 6).

#### IV. RESULTS

We solve for the liquid of LJ dumbbells the semischematic equations introduced in Sec. II using as inputs of the calculation the static structure factor  $S_q$  as obtained from the simulation (Figs. 2,3) and the COM number density  $n = 0.719$  at  $T^{MD} = 0.477$ . By solving Eq.5 on a grid of 300 equispaced  $q$  vectors, we find that the condition  $T_c^{MCT} = T^{MD}$  fixes the value of  $\chi_R$  to 1.17, which suggests that the coupling between COM and angular degrees of freedom in LJ dumbbells increases the COM memory function about 20%. If compared to the value  $\chi_R = 1.93$  found for SPC/E water [8,13], this result highlights the weaker hindering effect of the rotational motion in a liquid of LJ linear molecules with respect to the strong one observed in an hydrogen-bonded network-forming liquid. In water the highly energetic hydrogen bonds build up the network structure which is responsible for the caging of the molecules in the glass phase. The motion of the COM of the molecules is completely slaved to the breaking and reforming of the hydrogen bonds, i.e. it is definitely correlated to the angular dynamics.

The solution of Eq.5 for  $\chi_R = 1.17$  as a function of the wave-vector  $q$  is shown in Fig. 1 together with the COM non ergodicity parameters as calculated from the MD data. The theoretical  $f_q$  oscillates in phase with the MD data, but underestimates the amplitude, especially at large  $q$  vectors. The shoulder around  $q = 3$ , which may be attributed to the rotational-translational coupling, as the orientational correlator  $S_{11}^0(q)$  has a maximum at this  $q$ , is also underestimated. This notwithstanding, the semischematic  $f_q$  captures the  $q$ -dependence of the non ergodicity parameter as calculated from the MD data.

The simplicity of the semischematic equations allows us to study, besides  $f_q$ , also the complete time relaxation of  $\phi_q(t)$ . According to the theoretical predictions outlined in Sec. II we calculate the critical amplitudes

$h_q^{(1)}$  and  $h_q^{(2)}$  and the exponent  $b$  which rule the early  $\alpha$ -relaxation behavior (Eq. 7).

In Fig. 2, we present a comparison between the theoretical predictions of the semischematic model for the critical amplitudes  $h_q^{(1)}$  and  $h_q^{(2)}$  and the same quantities as calculated by fitting Eq.7 to the density-density correlation functions, i.e. with a quadratic fit in  $t^b$ . The fitting coefficients  $h_q^{(1)}/\tau^b$  and  $h_q^{(2)}/\tau^{2b}$  can be compared with the theoretical critical amplitudes after fixing, once and for all, the  $q$ -independent time scale  $\tau$ , introduced by the scale invariance of Eq. 2. The agreement is satisfactory in a wide range of  $q$  values. The theoretical value for the exponent parameter, as calculated from Eq. 9, is  $\lambda = 0.63$  to be compared with  $\lambda = 0.76$  as obtained by the simulation, i.e. the difference between the two is about 15%. This yields a theoretical critical exponent  $b = 0.75$ , while the exponent calculated from MD data is  $b = 0.55$ . In the case of SPC/E water the theoretical and MD values of  $b$  coincide within the numeric error. Such finding is consistent with the remarkable agreement of the non ergodicity parameters over both the relevant peaks of the structure factor.

The comparison between MD data and prediction of the semischematic model can be extended to the long time region. We solve the complete dynamic set of equations (2) in the whole  $q$  range [14]. We fit the stretched exponential law (Eq. 6) to the long time relaxation (late  $\alpha$ -region) and we compare the obtained amplitude  $A_q^K$ , relaxation time  $\tau_q^K$  and stretching exponent  $\beta_q^K$  with the corresponding quantities as calculated by fitting the MD relaxation. The comparison of the complete  $q$  dependence of  $A_q^K$ ,  $\tau_q^K$  and  $\beta_q^K$  is shown in Fig. 3. The theoretical and numerical relaxation times are in perfect agreement. Less satisfactory, as in the case of water, is the theoretical prediction for  $\beta_q^K$  for which the theory provides the correct qualitative  $q$ -dependence, but failing in amplitude up to 30%. The error in the values of the stretching exponents is expected on the basis of the drastic simplification adopted in the semischematic approach, which condensate the coupling between the infinite set of angular correlator and the COM correlator. Indeed, in phenomena in which the decay of correlation results from the sum of several independent relaxation processes, a smaller  $\beta$  indicates a wider distribution of relaxation times [15]. As expected  $A_q^K$  has the same behavior as  $f_q$  both for theory and simulation.

The choice of the dumbbell liquid is particularly interesting because it allows a comparison between the theoretical predictions of the semischematic model and those of MMCT which provides a deeper understanding of the basic approximation in the model, i.e. the assumption that the coupling between the COM and angular degrees of freedom can be quantified in a multiplicative  $q$ -independent factor  $\chi_R$ . The comparison requires a certain degree of care, because of the difference in the theo-

retical estimate of  $T^{MMCT}$ , rather different from  $T_c^{MD}$ . Indeed, while in the case of the semischematic model the MD and the theoretical  $f_q$  are evaluated at the same temperature, in the case of MMCT, the non ergodicity parameters are calculated using as inputs the structure factors from the simulations *but* evaluated at temperatures different from  $T_c^{MD}$ . Fig. 1 reports the COM MMCT non ergodicity parameters obtained in the approximations of diagonality and  $l \leq 2$  for the freezing of the COM dynamics only, and for the freezing of both COM and angular degrees of freedom.

A better insight into the comparison between the different theoretical approaches can be performed studying the non ergodicity parameter as predicted by the semischematic model at  $T_r^{MMCT}$ . Keeping fixed once and for all the coupling  $\chi_R = 1.17$ , we can solve Eq. 5 with the memory function Eq.3. With this choice of temperature the COM dynamics is in a deep glassy phase, both in the semischematic and MMCT descriptions. Thus, being in a non ergodic phase, the COM dynamic structure factor has a finite long-time limit, which is shown in Fig. 1. The semischematic (long dashed line) and MMCT (dotted line) predictions are in perfect agreement. This result can be enlightened by the comparison of the long time limits of the semischematic memory function  $m_q$  and the COM MMCT memory function  $[M_{00}^0(q)]^{TT}$  at  $T_r^{MMCT}$  (Fig. 4). We recall that the angular correlators contribute to  $[M_{00}^0(q)]^{TT}$  as well as the COM correlator, while the semischematic  $m_q$  is ruled only by the COM  $S_q$  and the value of  $\chi_R$ . Thus, the semischematic model gives rise to the complete functional dependence of the COM memory function on the rotational relaxation in a very simple way, i.e. taking into account only the functional dependence on the COM correlator and summarizing all the remaining coupling in the effective  $\chi_R$ . This means that the COM dynamics predicted by the semischematic model almost coincides with the corresponding predictions of MMCT in the diagonalization approximation. Furthermore the model has the advantage that the complete time evolution of the COM correlator can be calculated with current computational resources.

## V. CONCLUSIONS

A theoretical (but relatively simple) description of the COM dynamics in a molecular supercooled liquid is a relevant task which is recently focusing a lot of efforts. The situation recalls the early day of the MCT for simple liquids, when the dynamical equations were known but the exact numerical solutions were too difficult to handle. In that situation, simple approximations giving rise to a solvable set of equations were proposed and carefully studied. This class of approximations, which is still extensively used to interpret in a simple way experimental results [16,17], arises from the basic assumption

that the  $q$ -dependence of  $S_q$  can be reduced to a single representative  $q_0$  vector, i.e.  $S_q \propto \delta(q - q_0)$  [18]. In this approximation, which is named *schematic model*, the  $q$ -dependence is abandoned in favor of an exact description of one or two representative correlators. In the same spirit, the *semischematic* model provides a method for studying the complete  $q$ -dependence of the COM dynamics, neglecting the angular degrees of freedom which are condensed in a single  $q$ -independent parameter  $\chi_R$ .

Notwithstanding the drastic approximation intrinsic in the proposed approach, we have shown in this Article that the model captures the essential ingredients of the  $q$  dependent static and dynamic features of the COM  $\alpha$ -relaxation. The predicted non ergodicity parameter, relaxation time and stretching exponent oscillate in phase, the critical amplitudes out of phase, with the COM structure factor, i.e. the model predicts the same qualitative behavior observed in the simulation. The quantitative agreement with the MD data for  $f_q$ ,  $h_q^{(1)}$ ,  $h_q^{(2)}$  and  $\tau_q$  is satisfactory, especially for  $q$  vectors close to the maximum of  $S_q$ , while the stretching exponent  $\beta_K$  is overestimated. This reflects the major weakness of the approach but at the same time clearly indicates the role played by the angular degrees of freedom in controlling the dynamical evolution of the center of mass. If the present observations are discussed together with the semischematic analysis of the dynamics of SPC/E water, a model which mimics a liquid of strong directional hydrogen bonds, it gets obvious that the value of  $\chi_R$  is a measure for the strength of the roto-translational coupling.

The comparison between the semischematic model and the MMCT approximate solutions for the non ergodicity parameter and the memory function also supports the validity of the assumption of a  $q$ -independent  $\chi_R$ . Moreover, the coincidence of the theoretical critical  $T$  and the MD one, opens the way to precise comparisons between theory and experiments. Differently from the MMCT, the only required input in the model is the COM  $S_q$ , a quantity which can be experimentally measured by suitable designed neutron or x-rays scattering experiments [19].

## VI. ACKNOWLEDGMENT

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[1] W. Götze, in *Liquids, Freezing and the Glass Transition*, Eds.: J. P. Hansen, D. Levesque and J. Zinn-Justin, Les

- Houches. Session LI, 1989, (North-Holland, Amsterdam, 1991).
- [2] W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
  - [3] For recent reviews see for example C.A. Angell, Proc. 1996 Enrico Fermi Summer School in Physics, Italian Physical Society, in press. R. Schilling in *Disorder Effects on Relaxation Processes*, Eds. R. Richert and A. Blumen (Springer, Berlin 1994).
  - [4] T. Franosch, M. Fuchs, W. Götze, M.R. Mayr and A.P. Singh, *Phys. Rev. E* **56** 5659 (1997).
  - [5] R. Schilling and T. Scheidsteger, *Phys. Rev. E* **56** 2932 (1997). T. Scheidsteger and R. Schilling, *Phil. Mag.* **76** 305 (1998).
  - [6] C. Theis, Diplom Thesis Johannes Gutenberg Universität (1997).
  - [7] C. Theis and R. Schilling, proceedings of the 3rd International Discussion Meeting on Relaxation in Complex Systems, Vigo (1997), to be published in *J. Non-Cryst. Solids*.
  - [8] L. Fabbian, F. Sciortino, F. Thiery and P. Tartaglia, *Phys. Rev. E* **57** 1485 (1998).
  - [9] S. Kämmerer, W. Kob and R. Schilling, *Phys. Rev. E* **56** 5397 (1997). S. Kämmerer, W. Kob and R. Schilling, unpublished.
  - [10] Usually, the predicted MCT critical temperature  $T_c^{MCT}$  (or critical density) is higher (lower) then the corresponding “exact” critical temperature  $T_c^{MD}$  calculated numerically via MonteCarlo or MD simulations. Comparisons between theoretical predictions and numerical results are affected by such inevitable difference in temperature (or density). Indeed, the structure of the liquid at which MCT would predict the dynamical transition may be rather different from the structure of the liquid at  $T_c^{MD}$ . The phase relations between  $q$  dependence of  $S_q$  and the  $q$  dependence of  $f_q$ ,  $h_q^{(1)}$  and  $h_q^{(2)}$  observed at  $T_c^{MD}$  may be different from the one at  $T_c^{MCT}$ . Moreover, the Lamb-Mossbauer factor, defined as the non-ergodicity factor for the self density correlation, is strongly  $T$  dependent. Thus extreme care is requested on comparing MCT predictions and numerical findings if evaluated at different  $T$ .
  - [11] T. Franosch, M. Fuchs, W. Götze, M.R. Mayr and A.P. Singh, *Phys. Rev. E* **55**, 7153 (1997).
  - [12] R. Schilling and C. Theis, private communication.
  - [13] F. Sciortino, P. Gallo, P. Tartaglia, S.-H. Chen, *Phys. Rev. E* **54** 6331 (1996). F. Sciortino, L. Fabbian, S.H. Chen and P. Tartaglia, *Phys. Rev. E* **56** 5397 (1997).
  - [14] We use the numerical algorithm described in A.P. Singh, Ph.D. Thesis, Technischen Universität München, (1997). See also W. Götze *J. Stat. Phys.* **83** 1183 (1996).
  - [15] F. Sciortino and P. Tartaglia, *Physica A* **236**, 140 (1997).
  - [16] T. Franosch, W. Götze, M.R. Mayr and A.P. Singh, *Phys. Rev. E* **55**, 3183 (1997).
  - [17] C. Alba-Simionesco and M. Krauzman, *J. Chem. Phys.*, **102** 6574 (1995).
  - [18] E. Leutheusser, *Phys. Rev. A*, **29**, 2765 (1984).
  - [19] See for example A. Tölle, H. Schober, J. Wuttke and F. Fujara, *Phys. Rev. E* **56** 809 (1997) and references therein.

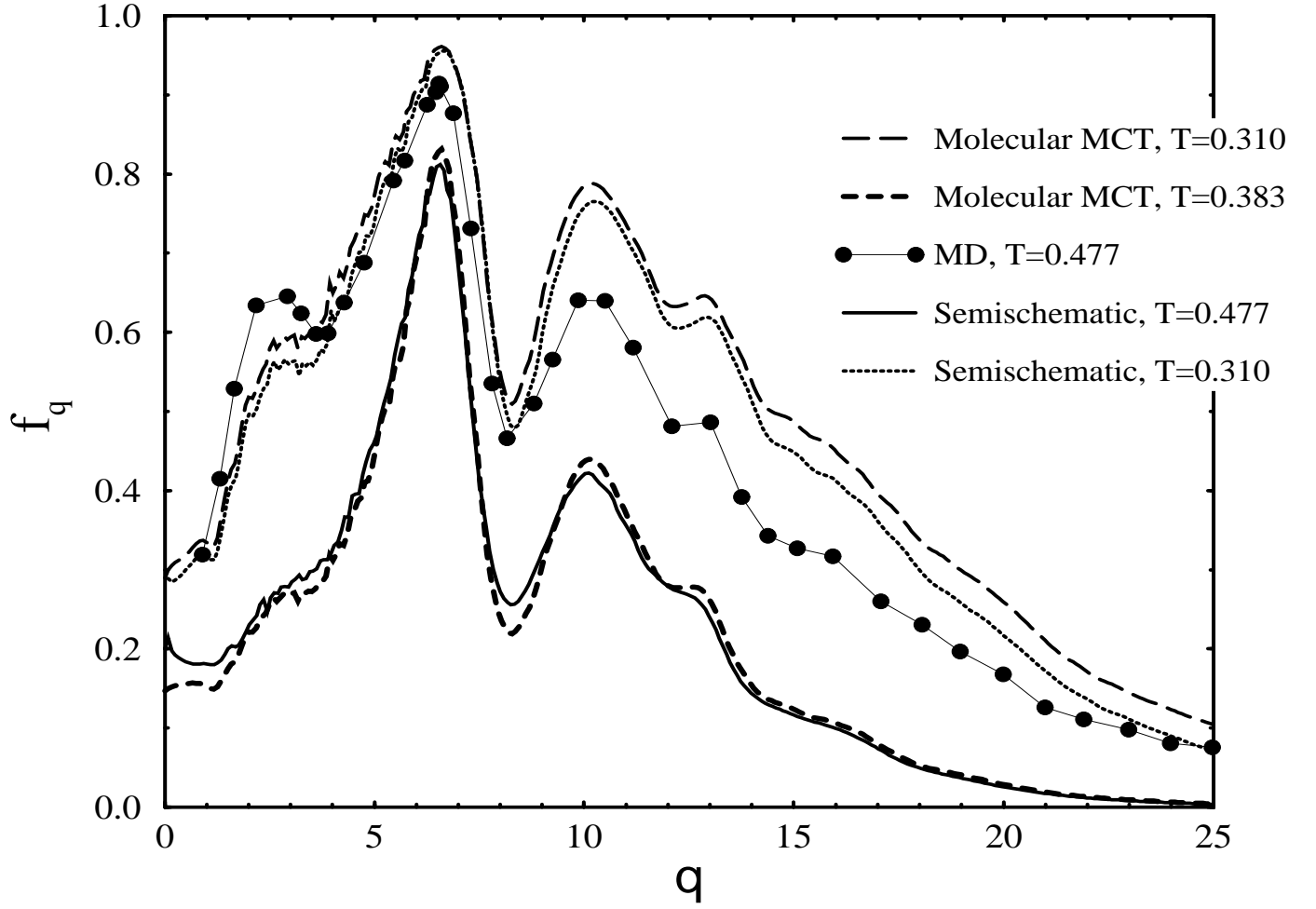


FIG. 1. COM non ergodicity parameter  $f_q$  as calculated by solving Eq. 5 (solid line) and as evaluated from the MD simulations [9] (symbols). For comparison also the COM non ergodicity parameters as predicted by MMCT are reported at two different temperatures (dashed lines). The dotted line shows  $f_q$  as predicted by the semischematic model at  $T = 0.310$ . The unit of  $q$  is  $2\pi\sigma_{AA}^{-1}$  while the unit of temperature is  $\epsilon_{AA}$  (setting  $K_B = 1$ ). The MMCT curves are from Ref. [6].

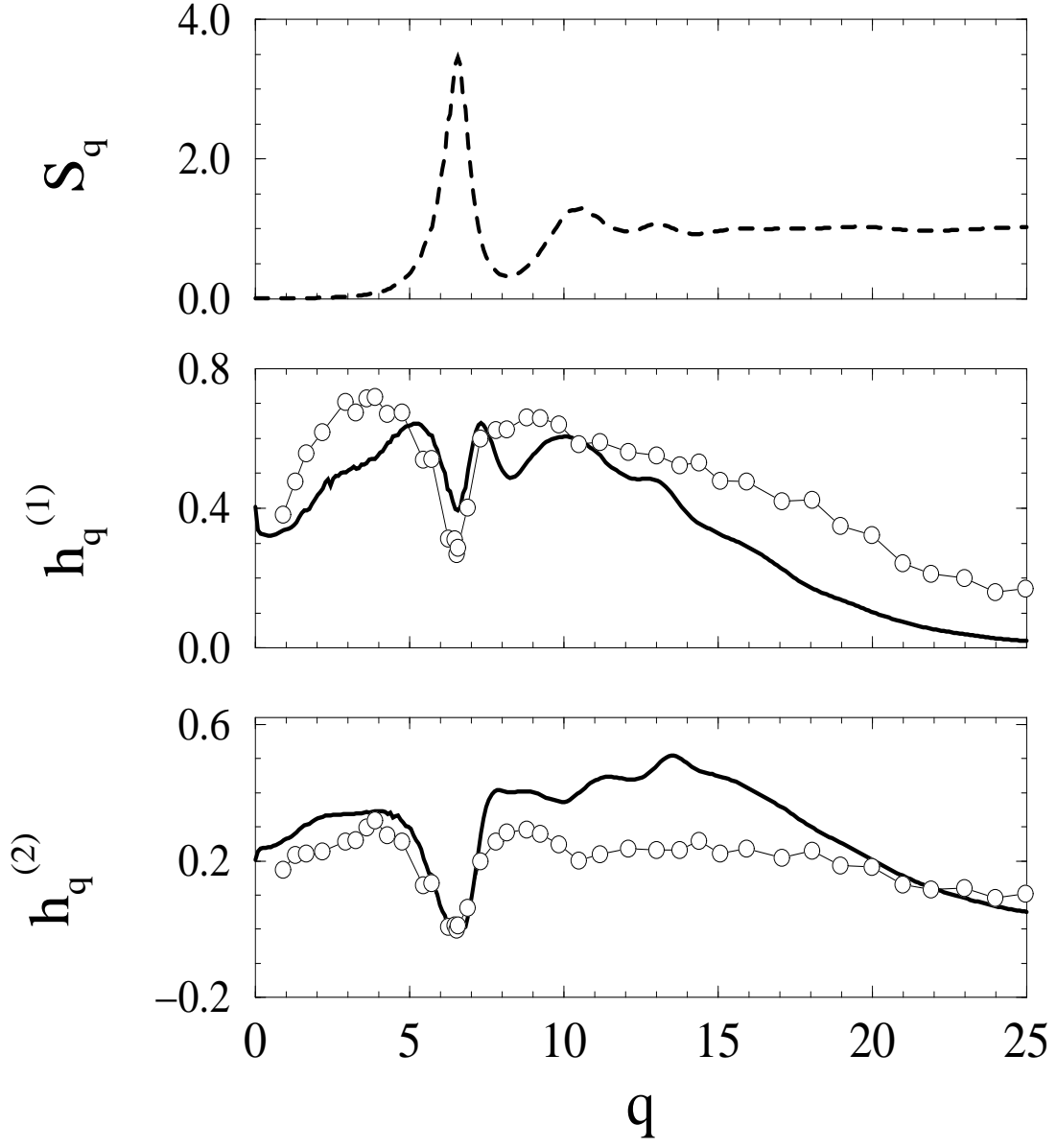


FIG. 2. Critical amplitudes  $h_q^{(1)}$  and  $h_q^{(2)}$  in the von Schweidler law Eq.7 as predicted by the semischematic model (solid lines) and as calculated from the MD data (symbols). The static structure factor  $S_q$  used as input of the theoretical calculation is also shown. The unit of  $q$  is  $2\pi\sigma_{AA}^{-1}$ .



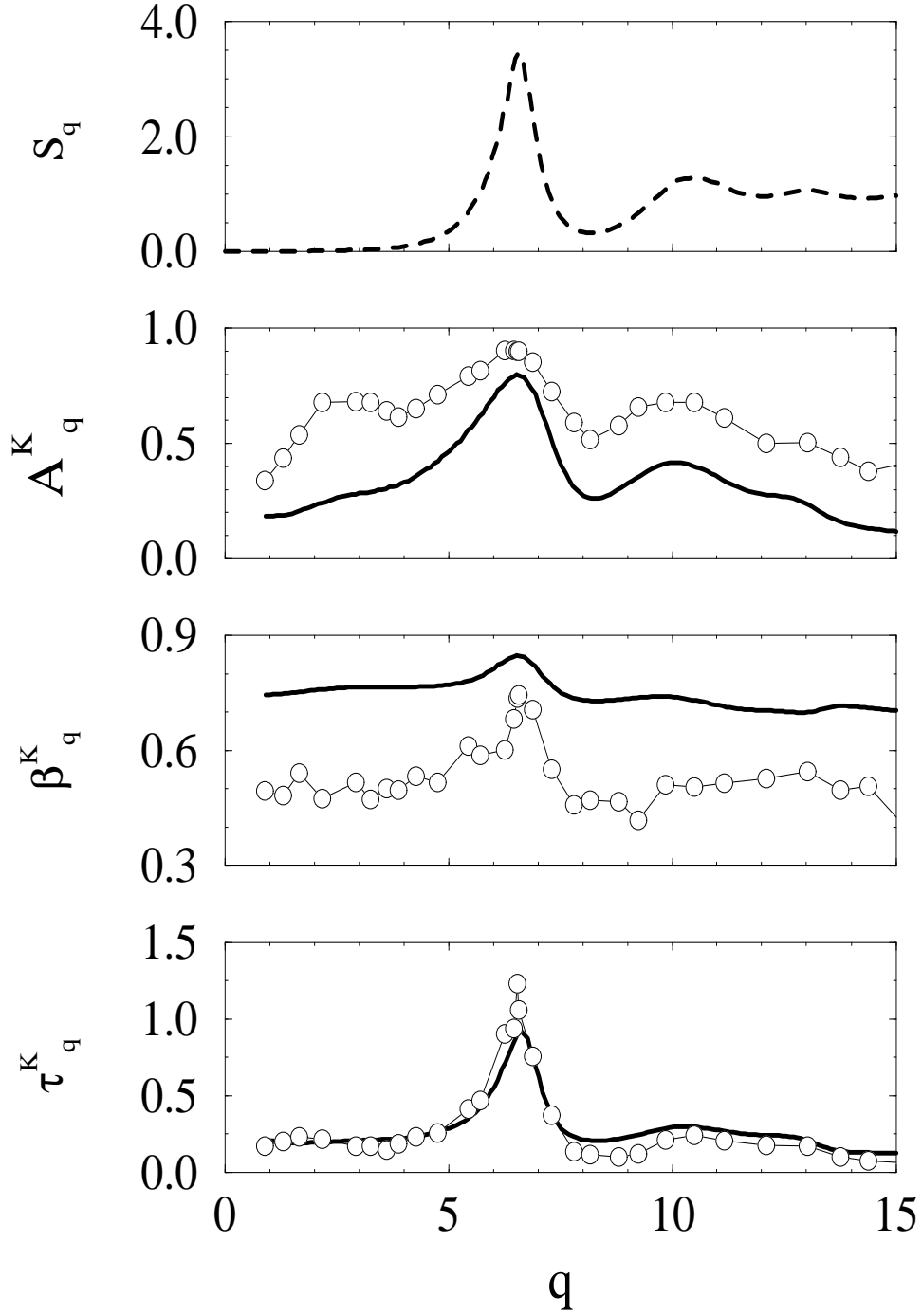


FIG. 3. Amplitude  $A_q^K$ , stretching exponent  $\beta_q^K$  and relaxation time  $\tau_q^K$  in the Kohlrausch-William-Watts law Eq. 6. Lines are obtained fitting Eq. 6 to the exact time dependent solution of Eq. 2 while symbols are evaluated fitting the same law to the MD data. The MD time unit for  $\tau_q^K$  is  $10^5((\sigma_{AA}^2 m)/(48\epsilon_{AA}))^{1/2}$  while the MCT relaxation times are arbitrarily scaled. The unit of  $q$  is  $2\pi\sigma_{AA}^{-1}$ . The static structure factor is shown as reference.

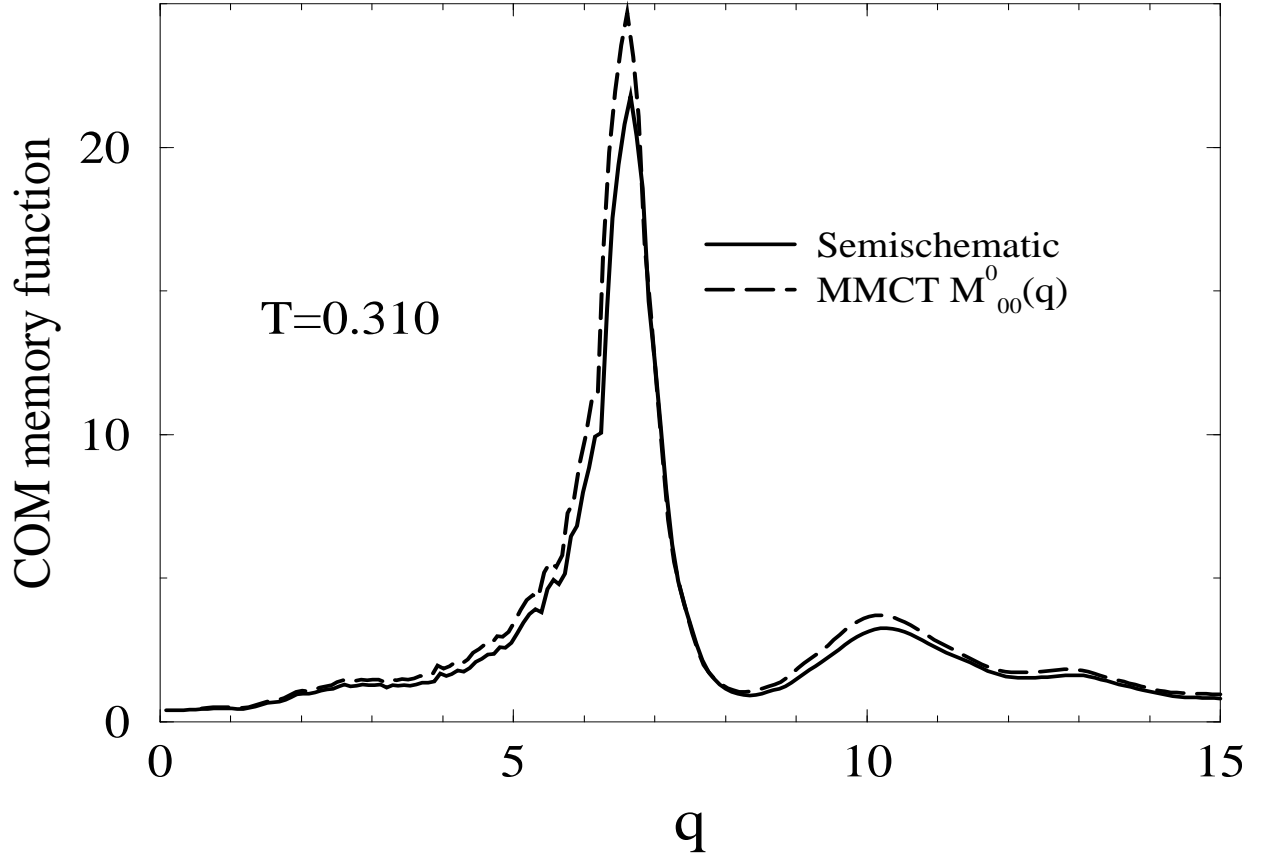


FIG. 4. COM memory function as predicted by the semischematic model Eq. 3 (solid line) and by MMCT (dashed line) at  $T_r^{MMCT} = 0.310$ . The unit of  $q$  is  $2\pi\sigma_{AA}^{-1}$  while the unit of temperature is  $\epsilon_{AA}$  (setting  $K_B = 1$ ).